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Cementing Reactions in the Hazardous Waste Environment

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16. ABSTRACT

The use of chemical grout for bottom sealing waste sites requires careful consideration of interfering reactions from contaminated soil or ground water. The cementing reactions in the acrylates and urethanes are very specific. The presence of reducers, oxidizers and complexors can make the grouting solution ineffective. Sodium silicate grouts that form by gel formation from a soil are not affected by oxidizing or reducing compounds. They are however sensitive to pH and the concentration of divalent and trivalent cations. The major problem with silicate grouts is accelerated setting which prevents the grout from penetrating the zone being sealed. The variety of possible grout/waste reactions is so broad that field testing with water and soil (or sediment) samples from the zone to be grouted is the most practical approach to selecting grout formulations and designing the grout program.

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Cementing Reactions in the Hazardous Waste Environment

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INTRODUCTION

Cementitious and chemical grouts have historically been used to control the movement of ground water and to reduce the permeability of soils or porous geologic media. Active control systems such as dewatering wells and water injection wells are generally used with any grout barrier designed for ground-water control.

Current requirements for controlling the movement of contaminated ground water and reducing the permeability of contaminated soils and wastes have led to the investigation of the applicability of standard ground water control techniques to hazardous waste sites. Chemical contaminants in the ground water or soil at a waste site can seriously interfere with the gelling or cementing reactions that must take place for the grout seal to solidify.

These adverse reactions can include:

(1) Destruction or deactivation of polymer or prepolymer materials in the grout.

(2) Destruction of initiators or accelerators needed in the gelling (polymerization) reaction.

(3) Acceleration of the polymerization reaction to a degree that prevents the proper injection of grout, because the grout viscosity rises too rapidly.

After polymerization has taken place, the solid grouting material is much less reactive. While specific durability problems may exist, hydrologic

techniques such as withdrawal of contaminated water and injection of clean water can be used to minimize exposure of the grout barrier to aggressive chemical wastes. The thickness of a grout barrier and the presence of non-reactive filler materials such as quartz sand and clays slow chemical attack on a barrier once it is in place.

Most cementing, setting or gelling reactions associated with grouts have specific requirements with regard to the pH, oxidation-reduction state or reactivity of the systems in which they will operate. The presence of industrial waste contaminants in the soil and ground water under a site can interfere seriously with these gelling reactions preventing the formation of any insoluble materials that might reduce sediment permeability[1].

The purpose of this paper is to examine the chemical reactions that are involved with three potentially useful chemical grout systems (acrylates, urethanes and silicates) and to indicate the nature of the interfering reactions that can occur. Strategies are developed that can be employed to overcome interfering materials and allow grout application under unfavorable conditions.

APPLICATION OF CHEMICAL GROUTS

Chemical grouts are a class of soluble compounds that, when pumped or injected into soils or particulate waste, will polymerize or gel to form solids that fill spaces between particles, reduce permeability and increase soil cohesion. Chemical grouts have advantages over bentonite clay or cement grouts in that chemical grouts can be formulated to have very low viscosities (near that of water) and can be injected into fine-grained materials where suspended grouts (cement and clay) cannot be used. The most widely used chemical grouts are acrylates, urethanes and silicates.

Acylate Grouts

Polyacrylic acid and other water-soluble acrylic polymers have a wide range of applications and their properties (hardness, adhesion etc.) can be varied by modifying chemical groups attached to the acrylate polymer (Figure 1). In a direct polymerization reaction, the acrylic acid monomer is mixed with water, potassium persulfate (a polymerization initiator) and sodium thiosulfate (an activator)[2]. A typical polymerization initiator is an oxidizer that reacts with the monomer to break the molecule and form charged fragments (free radicals) that can start the monomer linking. An activator is a chemical reducing agent that can scavenge oxygen that might inhibit polymer formation and operate to produce more free radicals than an oxidizer alone will provide[3]. Initiators and activators are supplied in relatively small concentrations (200-1000 ppm) and can be relatively easily destroyed. For example, even common reducers such as ferrous iron can destroy potassium persulfate; hexavalent chromium can destroy sodium thiosulfate. Polyvalent metals in solution can complex and precipitate acrylic acid monomer. Acrylic acid can also form very stable complexes with clay, that can make the monomer unavailable for grouting. A wide variety of industrial waste constituents can slow or stop acrylate polymer formation.

Urethane Grouts

Polyurethanes are polymeric compounds formed by reaction of an diisocyanate with an organic compound containing two or more attached groups with active hydrogens (Figure 2). Typically the polyurethane grout is supplied as a short-chain, low-viscosity polymer (polyurethane prepolymer). The prepolymer is prepared in a solution with excess

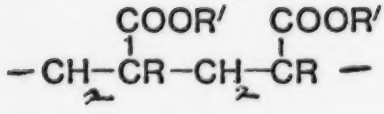

Figure 1.

Diagram of a simple acrylic polymer. R is H or CH_3. R′ is H, CH_3, CH_2H_5, NH_4, or alkali metals.

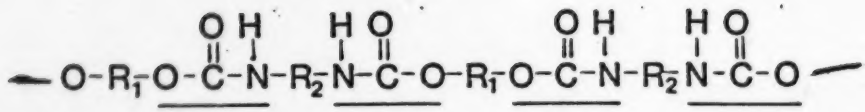

Figure 2.

Diagram of a simple linear urethane. R_1 and R_2 are organic radicals that can vary depending on the specific urethane formulation. The characteristic urethane linkages are underlined.

diisocyanate and has isocyanate functional groups on either end of the molecule. Final polymerization occurs when the isocyanate groups react with water and long polymer chains form. Generally amines, bases and metal compounds are used to increase the rate of polymerization. Acids and acid chlorides slow the polymerization reaction. The acid is not considered to directly affect the prepolymer, but the acid destroys any base that would act as a catalyst to promote polymer formation[4]. Ammonia and ammonium hydroxide also strongly retard grout set, but appear to act directly on the prepolymer, reacting with the terminal isocyanate to form urea. Fine-grained solids act as diluants and can slow; but generally do not stop, polymer formation[5].

Sodium Silicate Grouts

Sodium silicate grouts use the formation of silica gel to reduce permeability of sediments. Most sodium silicate grouting operations use a one-solution process where sodium silicate is mixed with a gelling or setting agent (such as sodium bicarbonate, formamide, sodium aluminate, calcium chloride, dilute hydrochloric acid or copper sulfate) and an accelerator (generally a second setting agent from the list above). For example, the setting agent formamide can be used with an accelerator, such as sodium aluminate to produce a rapidly setting gel. Salts of weak acid have also been used as setting agents. Specific salts include sodium bisulfite, sodium borate, potassium oxalate and sodium aluminate. The weak acid salt setting agents maintain an alkaline condition in the injected sediments and are generally favored in grouting for water control[6].

Sodium silicate is an unusual chemical grout in that polymerization occurs when the silicate sol is broken and a gel forms. Three-dimensional

silica gel networks form from concentrated alkaline solutions if the pH is dropped below 7 or if salts are added when the pH is between 7 and 10^7. In most grouting work sodium silicate, in a concentrated alkaline solution, is used and salt or acid is generally mixed in to produce the gelling reaction. Major interferences in sodium silicate systems occur when acids or metal salts cause premature gellation which prevents proper grout injection. Strong bases can prevent gel formation by neutralizing acid and precipitating metal salts. If strong bases are present, the liquid silicate grout may remain in sol form and be flushed out by any ground-water movement.

TESTING CHEMICAL GROUT/WASTE INTERACTIONS

Where it is suspected that soil or ground water will alter the setting characteristics of grouts, an appropriate laboratory testing program can be developed to determine exactly what problems can occur. Samples of core material recovered from the horizon to be sealed can be mixed with selected grouts and the setting timed to determine if gellation retardation reactions occur.

When actual soil and water are not available, simulated waste solutions can be used (Figure 3).

Small-scale field tests, where a grout sample is injected in one boring and samples are recovered by putting a second boring through the grouted material, can also be undertaken. Cored samples of grouted media can be tested to determine if permeabilities are lowered to meet required specifications for the remedial action proposed. Where the layer to be sealed is relatively shallow (2-3 meters); it may be practical to excavate and recover an entire grout bulb (such as that shown in Figure 4). In deeper grout tests it may be possible to case the second boring

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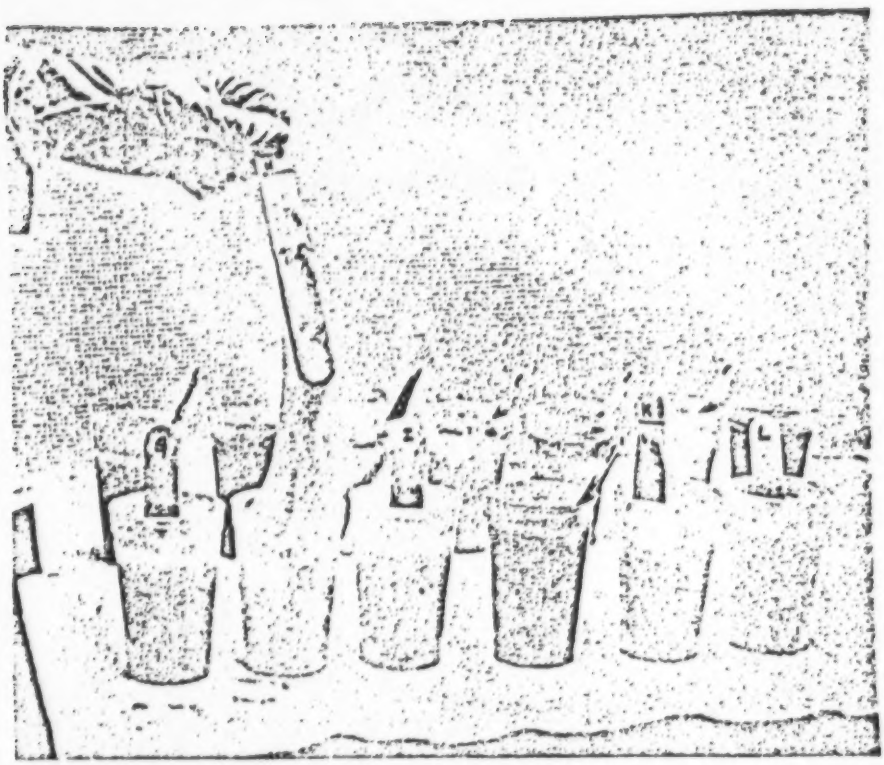

Figure 3.

Cup tests for grout/waste compatibility. Variations in set times and the condition of the grouts indicate the effects of simulated waste solutions.

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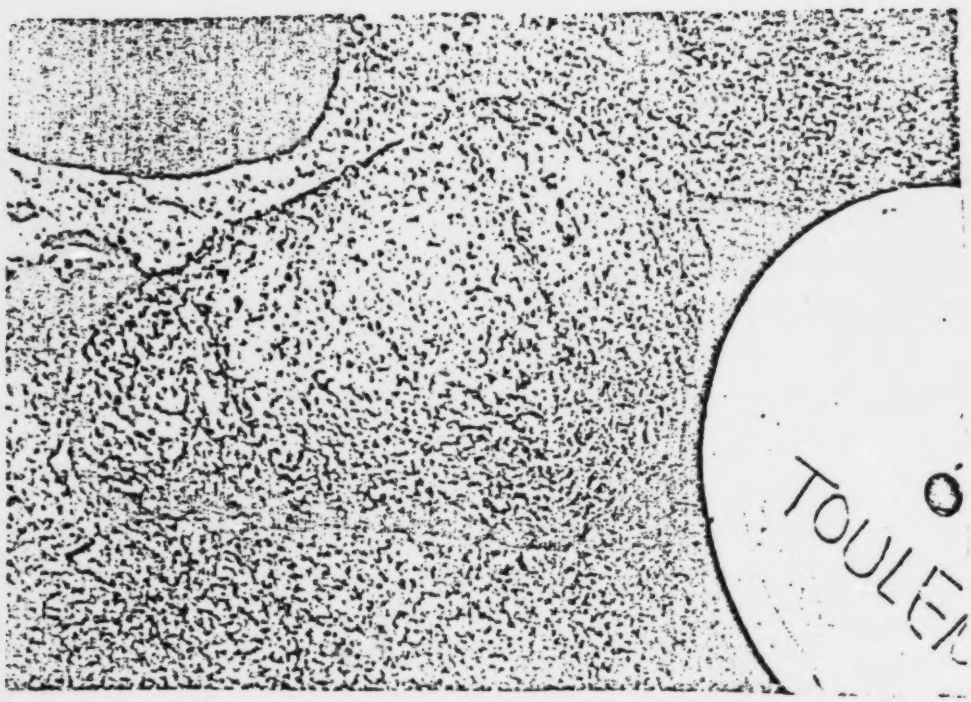

Figure 4.

Sodium silicate grout bulb recovered from a test grout injection into sand saturated with a toluene/water mixture. Samples of the grouted sand were used for permeability testing.

into the grouted horizon and conduct a pump test or a slug test to establish the effect of the grouting on formation permeability. Spalding, et al, report a test procedure where the grout injection holes are used for in-situ permeability measurements[8].

TECHNIQUES FOR GROUT INJECTION UNDER ADVERSE CHEMICAL CONDITIONS

Where water or soil chemistry prevents the setting or gelling of emplaced grout at a waste site; a number of possible solutions can be explored including:

(1) Examining the geologic material under the site for less contaminated, more compatible, horizons where grout will be effective.

(2) Forcing clean water into each hole to displace contaminated water from the areas around the grout injection horizon prior to grout placement.

(3) Selecting alternate grout formulations or grout types that are more compatible with the waste materials in the grouted horizons.

(4) Introducing chemical reagents in the borehole that will eliminate or destroy interfering compounds in the vicinity of the borehole during grout injection.

SUMMARY

The use of chemical grout for bottom sealing waste sites requires careful consideration of interfering reactions from contaminated soil or ground water. The cementing reactions in the acrylates and urethanes are very specific. The presence of reducers, oxidizers and complexors can make the grouting solution ineffective. Sodium silicate grouts that form by gel formation from a sol are not affected by oxidizing or reducing compounds. They are however sensitive to pH and the concentration of divalent and trivalent cations. The major problem with silicate grouts is accelerated setting

which prevents the grout from penetrating the zone being sealed. The variety of possible grout/waste reactions is so broad that field testing with water and soil (or sediment) samples from the zone to be grouted is the most practical approach to selecting grout formulations and designing the grout program.

Measures can be taken to select grouts that gel with the waste present, or displace or neutralize interfering materials. The durability of a grout seal is strongly dependent on the exposure of the solid grout to aggressive agents. An operating leachate collection system can be used to reduce the contact of contaminated water with the grout.

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